## SHIVAJI UNIVERSITY, KOLHAPUR

#### Question Bank For Mar 2022 (Summer) Examination

Subject Code: 81565 Subject Name: M.Sc. Part No-2(Sem-4) CBSC-Stereochemistry

8) 
$$\frac{1) BH_3 / THF}{2) H_2O / OH^{\Theta}}$$
?

10) OH 
$$\frac{\text{t-BuOOH, Ti(OiPr)}_4}{\text{CH}_2\text{Cl}_2, (+)DET}$$

12) 
$$(CH_2)_{n-1}$$
  $c=0 + HCN ?$ 

13) 
$$\stackrel{\stackrel{\stackrel{\bullet}{\text{N}}^{\bullet}(CH_3)_3}{\longrightarrow}}{\longrightarrow}$$
 ?

14) 
$$\begin{array}{c|c} & & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \begin{array}{c} & \text{i)} & \triangle \\ & & \\ & \text{ii)} & C_6 H_5 N(C_2 H_5)_2 \end{array}$$
?

15) 
$$Ni/H_2$$
 ? + ?

$$+ \begin{bmatrix} CH_2 \\ \parallel \\ 0 \end{bmatrix} - 2$$

$$+ BH_3 + H_3C \xrightarrow{CH_3} \xrightarrow{HOOH/OH} ?$$

21) OH 
$$\frac{\text{Ti(O-iPr)}_4, \text{L-(+)DET}}{\text{tert-BuOOH}}$$
 ?

$$\frac{\text{NaBH}_4}{\text{HOAc}} \rightarrow ? + ?$$

23) 
$$C_6H_{13}$$
  $Me$  ?

$$\begin{array}{c|c}
 & \text{CH}_3\text{OH} \\
\hline
 & \text{CH}_3\text{COONa}
\end{array}$$
?

26) 
$$Ar$$
  $NH_2$   $HNO_2$  ?

30) 
$$H$$
 +  $OCH_3$   $\Delta$  ?

31) 
$$\begin{array}{c} HO \\ \hline \\ C_6H_5 \end{array} \begin{array}{c} NH_2 \\ \hline \\ CH_3 \end{array} \begin{array}{c} H_2 \\ \hline \\ Pd \end{array} \begin{array}{c} ? \end{array}$$

32) 
$$\underset{\text{CH}_3}{\longleftarrow} \frac{\text{BH}_3/\text{THF}}{\underset{\text{H}_2\text{O}_2, \text{ OH, H}_2\text{O}}{\bigoplus}}$$
 ?

33) OH 
$$\frac{\text{(CH3)}_3\text{CCOOH}}{\text{Ti[OCH(CH}_3)_2]_4}$$
 ?

34) 
$$H$$
 +  $CH_3$   $CH_3$  ?

35) 
$$\sim$$
 COOBa  $\sim$  1)HNO<sub>2</sub>  $\sim$  ?

38) 
$$\begin{array}{c} \begin{array}{c} \text{CH}_3 \\ \hline \\ \text{CH}_3 \end{array} \begin{array}{c} \begin{array}{c} \text{BH}_3/\text{THF} \\ \hline \\ \text{OH}, \text{H}_2\text{O}_2 \end{array} \end{array} \begin{array}{c} ? + ? \end{array}$$

40) 
$$H + COOCH_3 \triangle$$
 ?

41) 
$$\begin{array}{c} \text{H}_{3}\text{C} \\ \text{OH} \end{array} \begin{array}{c} \text{(CH}_{3})_{3}\text{CCOOH} \\ \text{Ti[OCH(CH}_{3})_{2}]_{4} \\ \text{(+) DET} \end{array} ?$$

42) 
$$\begin{array}{c} C_6H_5 \\ H_3C \end{array} \begin{array}{c} C_6H_5 \\ CH_3 \end{array} \begin{array}{c} H_2 \\ Pd \end{array} \begin{array}{c} ? \end{array}$$

44) 
$$\begin{array}{c} H \xrightarrow{\text{CH}_3} & BH_3 \\ \hline & H_2O_2 / OH \end{array}$$
?

45) 
$$H + COOCH_3$$

$$47) \qquad + \qquad H_2N \qquad \qquad H_{MM}H \qquad Base \qquad ?$$

48) 
$$C_{6}H_{5}$$
  $C_{3}H_{7}$   $C_{3}H_{7}$   $C_{3}H_{4}$   $C_{3}H_{4}$ 

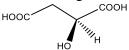
49) 
$$\begin{array}{c} O \\ H_3C \\ H_5 \end{array} \xrightarrow{H} \begin{array}{c} CH_3MgB_r \\ H_3O \end{array} ? + ?$$

50) 2 
$$hv$$
 ?

51) 
$$\frac{\text{LiAlH}_4}{\text{H}_2\text{O}}$$
 ?

- 53) Write the structure of most stable conformation of cis-1,4-di-t-butyleyclohexane.
- 54) -----is an arrangement in space of the atoms or groups around the asymmetric carbon.
- 55) What is Bredt's rule?
- 56) How is UV spectroscopic method useful to distinguish between cis and trans-Stilbene.
- 57) State the circular dichroism.
- 58) In biphenyls substitution of meta position tend to enhance racemization barriers by what is called as ----- effect.
- 59) In allenes central SP hybridized carbon contained ----- pairs of p-orbitals.
- 60) Draw the structure of cis and trans decaline.
- 61) How many methods are available for the determination of configuration of olefinic geometrical isomers?
- 62) Between a pair of cis and trans isomers which one shows the higher melting point.
- 63) In the reaction crystal, both benzene rings of biphenyl lie in the ----- plane.
- 64) What is the Alder rule?
- 65) Why the hydrolysis of tetra-methyl succinic acid ester with aqueous acid gives an anhydride and not acid?

- 66) What do you mean by optical rotatory dispersion?
- 67) How the chirality is determined?
- 68) Determine the configuration of the isomer of 2-hydroxysuccinic acid shown below.



- 69) Define the enantiomerism?
- 70) What is mean by the term meso compound?
- 71) Define the term stereoselectivity
- 72) The addition of a hydride donor to an aldehyde or to a ketone gives an -----.
- 73) Define the Spiranes?
- 74) Ring closing is easily possible when two functional groups which are on the -----side of the double bond.
- 75) What is stereoselective synthesis?
- 76) Why bridgehead Carbocation is not stable?

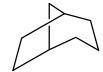
- 77) Why maleic acid is more soluble than fumaric acid in water?
- 78) In the crystal, both benzene rings of biphenyl lie in the same plane. Say true or false.
- 79) What reactions are stereospecific?
- 80) What does enantioselective mean?
- 81) Which isomer is more stable, cis-1,3-dimethylcyclohexane or trans-1,3-dimethylcyclohexane?
- 82) Assign the nomenclature to following compound.



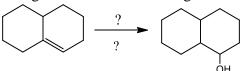
- 83) Define the atropisomerism?
- 84) Assign the nomenclature to following compound.



85) Assign the nomenclature to following compound.



86) What reagents are needed to bring about the following transformation?



87) How do you assign the configuration to trisubstituted olefins?

#### **SECTION-I**

<u>Q2</u>

- a) Bromination of cyclohexene has been designated a stereoselective reaction. However, some chemists also term it stereospecific. Explain?
- b) 4-t-butyl cyclohexanone on reduction with sodium borohydride gives a diastereomeric mixture of alcohols. Is this reaction stereospecific or stereoselective? Explain.
- a) State and explain "Octant rule and Axial halo ketone rule".
- b) State and explain applications of ORD and CD curves.
- a) Explain the Cram's rule?
- b) Explain the energy versus dihedral angle for conformations of ethane.
- a) How one can carry out asymmetric reduction of carbonyl compounds?
- b) Explain the energy versus dihedral angle for conformations of 2,3-dimethylbutane.
- a) Explain the energy versus dihedral angle for conformations of n-propyl chloride.
- b) Discuss the conformations of 2,3-dimethylbutane.

#### <u>Q3</u>

a) Explain the asymmetric epoxidation of allylic alcohols.

b) Describe the effect of conformation on stability and reactivity involving in acyclic compounds w.r.t.

- i) Ionic elimination reactions
- ii) NGP reactions
- a) Explain the Klyne-Prelog terminology for torsion strain.
- b) Describe the conformational effects of semipinacolic deamination of 1,2-diphenyl-1-(p-chlorophenyl)-2-amono ethanol.
- a) what do you mean by stereoselective and stereospecific synthesis.
- b) Explain the methods of determining the configuration in cyclohexane.
- a) Predict the product and stereochemistry of following.

i) 
$$H \rightarrow OH \longrightarrow H_3BO_3$$
?

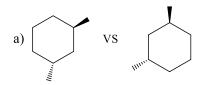
ii)  $H \rightarrow OH \longrightarrow CH_3$ 

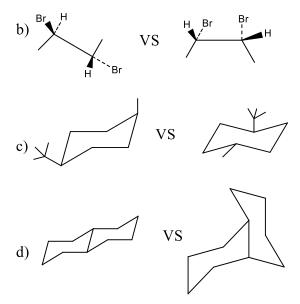
iii)  $H \rightarrow CH_3$ 
 $H \rightarrow H \longrightarrow CH_3$ 
 $H \rightarrow H \longrightarrow CH_3$ 

O

iii)  $H \rightarrow CH_3$ 
 $H \rightarrow H \longrightarrow CH_3$ 
 $H \rightarrow CH_3$ 
 $H \rightarrow CH_3$ 
 $H \rightarrow CH_3$ 
 $H \rightarrow CH_3$ 

- b) State and explain Curtin-Hammett principle.
- a) Explain the chair and boat conformations of cyclohexane.
- b) Explain the conformational analysis and reactivity of octalins.
- a) Discuss the stereospecificity and greater rate of formation of trans product compared to cis in the elimination of bromine by iodide ion from meso-2,3-dibromobutane and racemic mixture of 2,3-dibromobutane.
- b) Explain the conformational analysis and reactivity of decalols
- a) Define the relationship between the following pairs of molecules as identical, conformers, non-isomers, constitutional isomers, enantiomers and diaseteromers. Tell whether they are optically active or not.





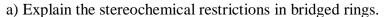
#### **Q4**

- a) Draw the conformations of perhydroanthracene and explain their stability.
- b) Give an account of the stereochemistry of Allenes.
- a) Draw the structures of cis and trans decalines and explain their stability.
- b) Discuss the stereochemistry of biphenyls.
- a) Illustrate the conformational analysis and reactivity of heptane.
- b) Give an account of the stereochemistry of allenes and spiranes.
- a) Discuss the Sharpless epoxidation with stereochemistry and mechanism.
- b) How do you calculate enantiomeric excess? Explain it with suitable example.
- a) Explain the cis and trans decalin with respect to difference in potential energy and nuclear magnetic resonance spectra .
- b) What is cotton effect curve? How many kinds of cotton effect curves are there? Describe them.
- a) Discuss the ease of ring formation as a function of ring size and the nature of substitution of the ring atoms.
- b) The applications of optical rotatory dispersion in assigning conformation and configuration of various molecules.

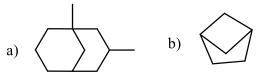
#### **SECTION-II**

#### <u>Q5</u>

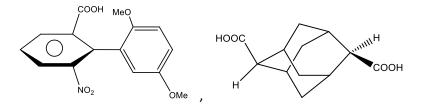
- a) Give the applications of ORD and CD curves.
- b) Describe the physical methods used to assign the configuration of diastereoisomers.
- a) Give an account of stereospecific and stereoselective synthesis.
- b) Give an account of various methods used for determining the configuration of acyclic ring system.



- b) Describe the various chemical methods you have studied to assign the configuration of geometrical isomers.
- a) i) Give the nomenclature to following bridged rings.



ii) Assign the R & S nomenclature to following compounds.



- b) Describe the various physical methods you have studied to assign the configuration of geometrical isomers.
- a) Discuss the determination and configuration of olefins using dipole moment, Melting Point and Boiling Point method.
- b) What is optical rotary dispersion? Explain the significance of cotton effect in determination of structure, conformation and configuration.
- a) Discuss the determination and configuration of olefinic geometrical isomers using ring closing and opening as well as chemical correlation method.
- b) Explain the stereochemical restrictions with suitable example.

#### **Q6**

- a) What is Bredt's rule? Explain with suitable example.
- b) Explain the dihydroxylation of olefins using Upjohn process.
- a) Explain the nucleophilic addition to carbonyl compounds using auxiliaries.
- b) Explain the different conformations of 1,4-cyclohexanediol.
- a) 4-t-butyl cyclohexanone on reduction with sodium borohydride gives a diastereomeric mixture of alcohols. Is this reaction stereospecific or stereoselective? Explain.
- b) Compound which are term optically active are capable and rotating the path and plane polarized light either clockwise or anticlockwise while those which are not optically active cannot do, so why?
- a) Illustratethe stereochemistry of Spiranes.

b) Predict the product with mechanism and stereochemistry of following reaction.

- a) Explain the conformations of 1,4-di-t-butylcyclohexane.
- b) Discuss the determination and configuration of olefins using spectroscopy methods.
- a) Assign the configuration to following compounds.

#### **Q7**

- a) Explain the following (Any four):
  - a) Axil haloketone rule
  - b) Types of ORD curves
  - c) Octant rule
  - d) Stereochemistry of bridged rings
  - e) NGP reactions
- b) Describe the relative reactivity of diastereoisomers.
- a) Discuss the stereochemistry of Spiranes.
- b) Draw the conformations of perhydroanthracene and explain their stability.
- a) What is cotton effect curve? How many kinds of cotton effect curves are there? Describe them.
- b) Cycloaddition of an unsymmetrically substituted diene and an unsymmetrically substituted dienophine can lead to regioisomers .Explain it with example.
- a) Explain the enantioselective alkylation of ketones via chiral oxazolidinone.
- b) Explain the concept of stereochemical restrictions with suitable example.
- a) Illustrate the stereochemistry of allene
- b) Illustrate the axial haloketone rule with suitable example.
- a) Discuss the determination and configuration of olefins using Melting/boiling point methods.
- b) Correctly substituted ortho biphenyls are chiral and rotation about the junction bond will racemize a pure enantiomer. Explain with examples.

Total No. of Pages: 4

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No.	

# M.Sc. (Part-II) (Semester-IV) (CBCS) Examination, April-2019 ORGANIC CHEMISTRY

## **Stereochemistry (Paper-XIV)**

Sub. Code: 61431

Day and Date: Wednesday, 03 - 4 - 2019

Total Marks: 80

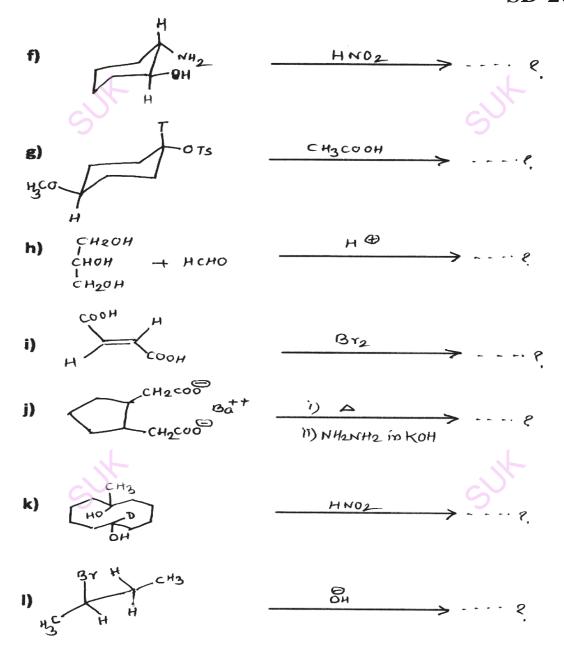
Time: 11.00 a.m. to 2.00 p.m.

**Instructions:** 

- 1) Attempt in all Five questions and answer to all Question should be written in the same answer book.
- 2) Question No. 1 is compulsory and objective type.
- 3) Solve any two questions from section-I and any two from section-II
- 4) All questions carry equal marks. (16 each)
- Q1) A) Predict the products and the stereochemistry in the following: (One mark each) [16]

b) 
$$(CH_2)_{\gamma_1-2} \xrightarrow{CH_2} \bigoplus_{CH_3} \bigoplus_{3}$$

P.T.O.



- B) Answer the following (One mark each):
  - a) What is an optical purity?
  - b) Draw the structures of cis- & trans decalins.
  - c) Draw erythro- & threo-forms of 3-bromo-2-butanol
  - d) What is trans-annular strain?



# **SECTION-I**

<b>Q2</b> ) a)	Explain the effect of the conformation on the reactivity of acyclic compounds w.r.t. following: [8]
	i) Molecular rearrangements
	ii) NGP reactions
b)	State & explain 'Curtain-Hammett principle' [8]
<b>Q3</b> ) a)	Draw the conformations of perhydroanthracene and explain their stability. [8]
b)	Explain the conformational effects in medium sized ring systems. [8]
<b>Q4</b> ) a)	Draw the shapes of five, Seven & eight member rings and explain their stability. [8]
b)	Answer the following: [8]
	i) Draw the structures of 3,4-diphenyl cyclobutane 1,2-dicarboxylic acid.
	ii) Explain with the suitable examples why the presence of alkyl group favors the ring formation?
	SECTION-II
<b>Q5</b> ) a)	Explain different methods of Chiral synthesis. [10]
b)	Explain the stereoselective synthesis with suitable examples. [6]
<b>Q6</b> ) a)	Describe various Chemical methods used to determine the configuration of diastereo (geometrical) isomers. [8]
b)	State and explain 'Octant rule with suitable examples. [4]
c)	What is 'axial haloketone rule?' [4]

#### **Q7**) Explain the following (Any four:)

[16]

- a) Configuration of biphenyls
- b) Stereochemistry of bridged ring systems.
- c) Methods of determining the configuration of isomers in alicyclic ring systems.
- d) Applications of O.R.D and C. D. curves
- e) Stereochemistry of allenes
- f) Reactivity of cyclohexane derivatives



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Total No. of Pages: 3



# M.Sc. (Part - II) (Semester - IV) (CBCS) Examination, November - 2018 ORGANIC CHEMISTRY

### **Stereochemistry** (Paper - XIV)

Sub. Code: 61431

Day and Date: Monday, 26 - 11 - 2018 Total Marks: 80

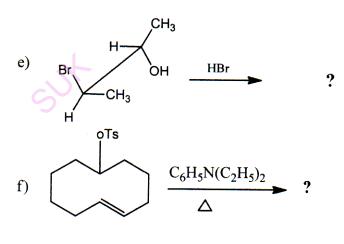
Time: 02.30 p.m. to 05.30 p.m.

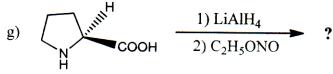
**Instructions:** 1) Question No.1 is compulsory.

- 2) Answer any two questions from each section.
- 3) Answers to the all the questions should written in the same answer book.
- 4) Figures to the right indicate marks.

Q1) A) Predict the products and the stereochemistry in the following. [16]

d) 
$$\frac{\text{t-BuOOH, Ti(OiPr)}_4}{\text{CH}_2\text{Cl}_2, (-)DET}$$
 ?





- B) Answer the following.
  - h) Write the structure of most stable conformation of cis-1,4-di-t-butylcyclohexane.
  - i) \_\_\_\_\_is an arrangement in space of the atoms or groups around the asymmetric carbon.
  - j) What is Bredt's rule?
  - k) How is UV spectroscopic method useful to distinguish between cis and trans-stilbene
  - l) State the circular dichroism.
  - m) In biphenyls substitution of meta position tend to enhance racemization barriers by what is called as \_\_\_\_\_ effect.
  - n) In allenes central SP hybridized carbon contained \_\_\_\_\_ pairs of p-orbitals.
  - o) Draw the structure of cis and trans decaline.
  - p) State the thermodynamic controlled reaction.

#### SECTION-I

		SECTION-I
Q2)	a)	Bromination of cyclohexene has been designated a stereoselective reaction. However, some chemists also term it stereospecific. Explain. [10]
	b)	Explain the concept of 'I' strain. [6]
Q3)	a)	Explain the asymmetric synthesis involving the hydroboration and catalytic hydrogenation reactions. [8]
	b)	Describe the effect of conformation on stability and reactivity involving in acyclic compounds w.r.t. [8]
		i) Ionic elimination reactions
		ii) NGP reactions
Q4)	a)	Draw the conformations of perhydroanthracene and explain their stability. [8]
	b)	Give an account of the stereochemistry of Allenes. [8]
		SECTION-II
Q5)	a)	Give the applications of ORD and CD curves. [8]
	b)	Describe the physical methods used to assign the configuration of diastereoisomers. [8]
Q6)	a)	Explain the term optical purity and enantiomeric excess. [8]
	b)	What is Bredt's rule? Explain with suitable example. [8]
Q7)	a)	Draw the shapes of five, seven and eight membered rings and explain their stabilities. [8]
	b)	Discuss the stereochemistry of Spiranes. [8]

